PAH Removal Using Soil and Sediment Washing at a Contaminated Harbor Site

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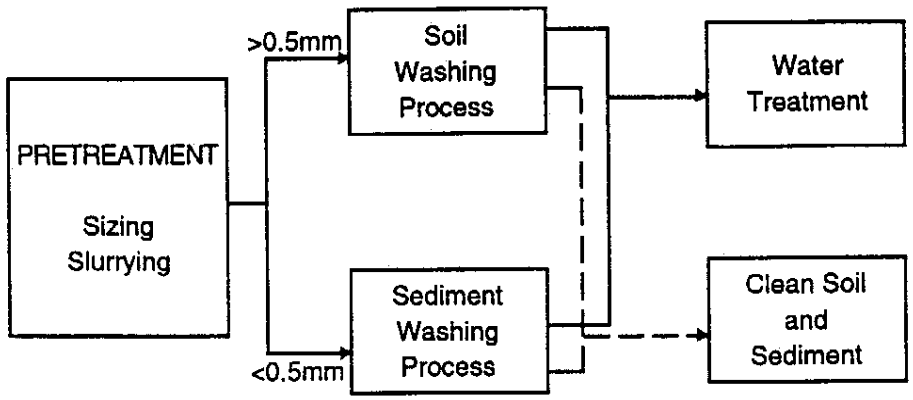
In tests conducted for the Canadian government on sediment from Thunder Bay Harbour, Ontario, the BioGenesis washing process was demonstrated to be effective in remediating contaminated harbor sediments. Removal efficiencies for 16 polyaromatic hydrocarbons (PAHs) in concentrations exceeding 4,000 parts per million averaged 90 to 95 percent in pilot tests. These results are significant because, until now, washing processes have not proven effective in cleaning the small-size particles of silt and clay that make up most underwater sediments. In Thunder Bay, 81 percent of the particles were less than 38 microns (medium silt) in size. The tests on Thunder Bay sediment were conducted under the auspices of the Contaminated Sediment Treatment Technology Program of Environment Canada's Wastewater Technology Centre. Thunder Bay Harbour is one of 43 "areas of concern" identified by the International Joint Commission of Great Lakes Water Quality.

BioGenesis Enterprises, Inc. has developed a soil and sediment washing process capable of cleaning heavy hydrocarbon pollutants (including crude oil, polyaromatic hydrocarbons (PAHs), fuel oils, and diesel) from most matrices. The process is applicable to a broad range of hazardous organics and metals, including harbor sediments. The company has demonstrated its large particle technology in the U.S. EPA Superfund Innovative Technology Evaluation (SITE) program and tested its sediment washing technology under the auspices of Environment Canada's Great Lakes Cleanup Fund and Wastewater Technology Centre's Contaminated Sediment Treatment Technology Program.

BioGenesis washing technology advances the state of the remediation art by solving three obstacles to widespread implementation of soil washing technology—inability to handle heavy pollutants, inability to wash small sediments, and the capital cost and relative immobility of large processing plants. Additionally, this technology incorporates synthetic biosurfactant chemicals that provide continuing remediation action after washing is completed. This article describes the technology and reports the results of U.S. and Canadian evaluation programs.

Exhibit 1. Soil and Sediment Washing Process Overview.



TECHNOLOGY DESCRIPTION

The BioGenesis soil washing process is an ex-situ, on-site extraction technology for organic pollutants and metals. **Exhibit 1** gives an overview of the total system. The process uses complex bioremediating surfactant blends, water, heat, mixing, and friction to clean soil and sediment. Two types of mobile equipment wash different particle sizes. A truck-mounted batch unit processing 40 yards an hour washes soil particles 0.5 mm and larger. A mobile, continuous flow unit can clean more than 80 yards an hour for sediment particles smaller than 0.5 mm.

Auxiliary equipment includes particle sizing equipment, tanks, dewatering and water treatment equipment, and a bioreactor. Extraction efficiencies range from 85 to 99 percent depending on the pollutant type, initial concentration, and soil/sediment type. **Exhibit 2** illustrates the sediment washing process for small particles and **Exhibit 3**, the soil washing process for larger particles.

Sediment Subsystem

The sediment washing machine is a continuous flow unit. Capacities of up to 80 to 100 cubic yards an hour are possible using parallel processing and multiple equipment.

Sediment is pretreated via grizzlies to separate debris not suitable for shredding. These oversize materials are diverted to the large particle washer for treatment. Material passing the grizzly flows to a shredder and then to pretreatment tanks. The shredded material is blended, heated, and mixed with water and biosurfactant chemicals. This forms a slurry.

The slurry then passes to a shaker screen separator that sizes particles into two streams. Material greater than 0.5 mm diameter is diverted to the large-particle soil washer. Material 0.5 mm and smaller continues to the sediment washer's feed hopper. From there the slurry is injected to the sediment collision chamber, where it collides with water and cleaning

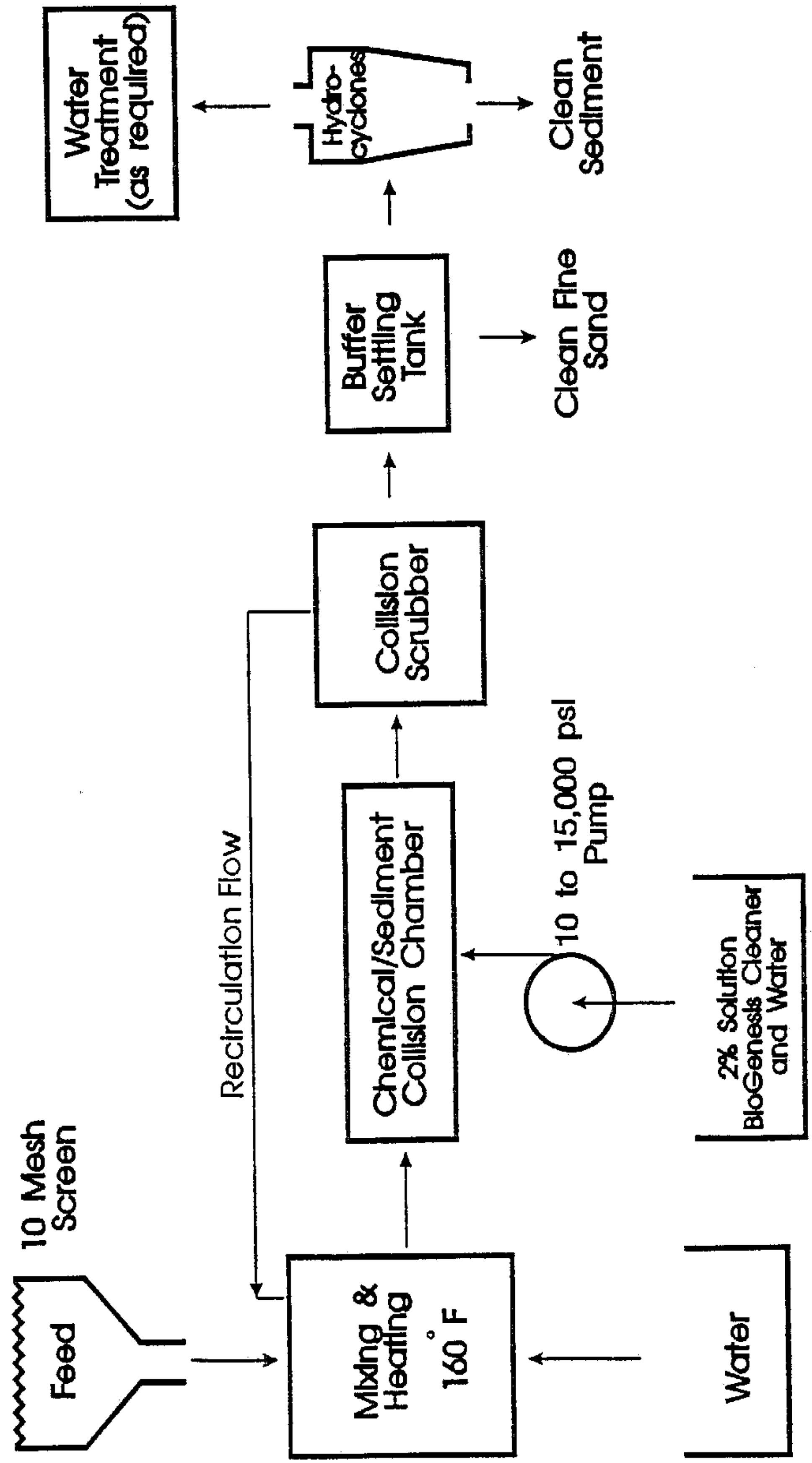


Exhibit 2. BioGenesis Sediment Washing.

Exhibit 3. BioGenesis Soil Washing.

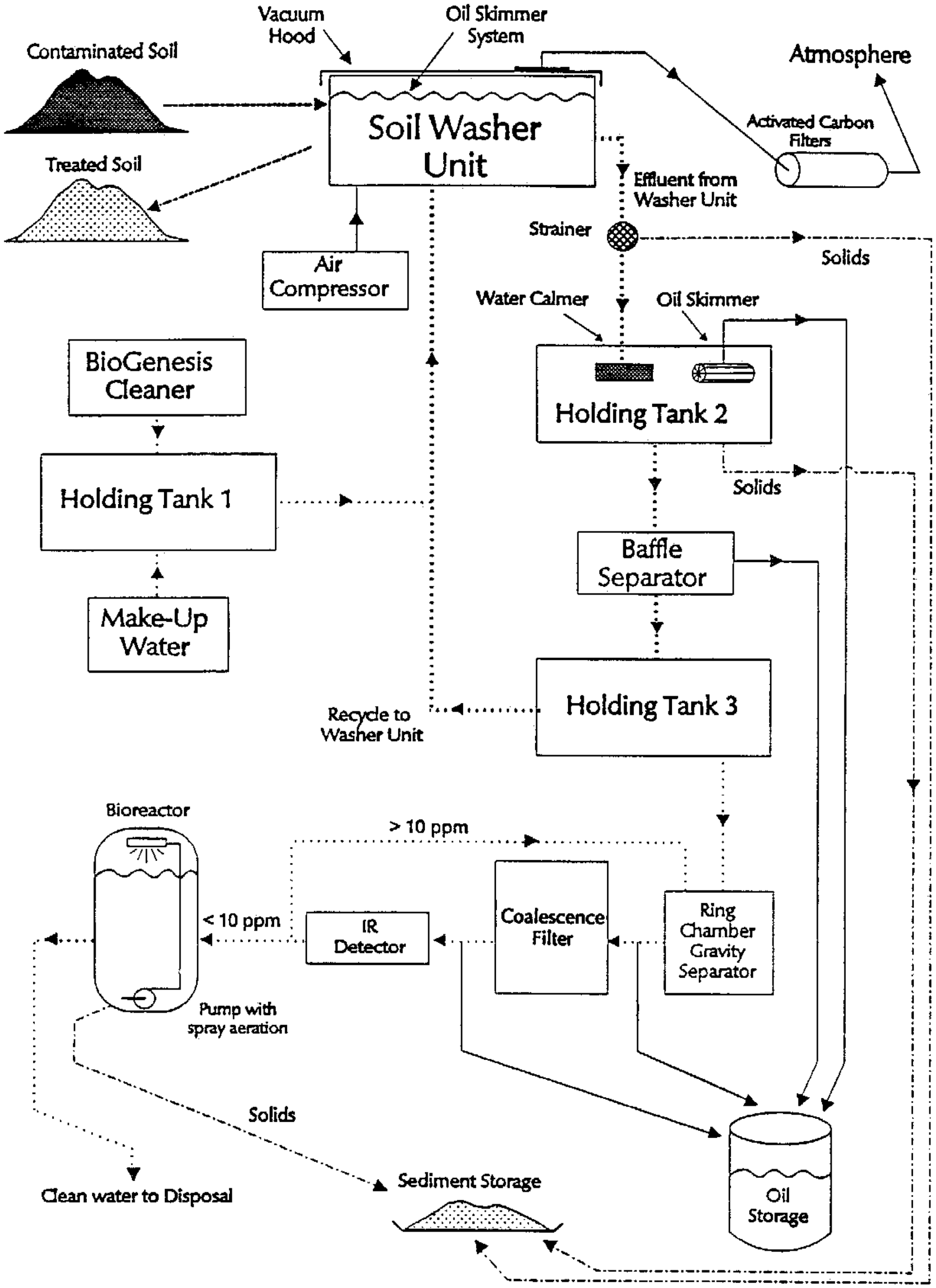
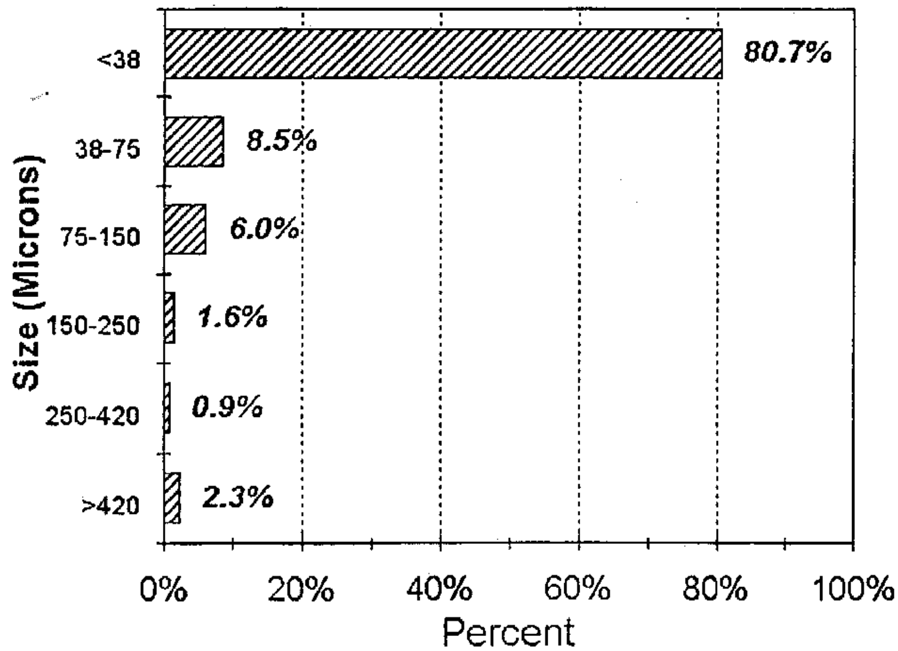


Exhibit 4. Particle Size Distribution of Thunder Bay Harbour Sediment.



chemicals at 10,000 to 15,000 psi pressure. This accomplishes primary loosening of the bonds between the pollutant and the particle.

After the collision chamber, the slurry flows to the collision scrubber, which ensures that the particles are thoroughly wetted. The scrubbing process further weakens the bonds between contaminant and particle. Normally, three collision chamber/collision scrubber sets are connected in series to accomplish successive washings. Following the last scrubber, the slurry passes through a buffer tank, where any large particles separate by gravity. The slurry then flows through hydrocyclone banks to separate solids down to 5 to 10 microns in size. The free liquid routes to a centrifuge for final solid-liquid separation.

All solids go to the clean soil pile, whereas all liquid is routed to wastewater treatment to remove organic and inorganic contaminants. Decontaminated water is recycled back through the process.

Soil Subsystem

The soil washing system for larger particles is a batch process with throughput capacity of up to 40 yards an hour. The system consists of a trailer-mounted gondola plumbed for air mixing, water/chemical addition, oil skimming, and liquid drainage. Water, cleaning chemicals, and soil are loaded into the gondola. Aeration nozzles in the bottom of the gondola feed compressed air to create the effect of a fluidized bed.

The resulting slurry is agitated by the aerators for about 30 minutes to release organic and inorganic contaminants from the soil particles. After mixing, a short settling period allows the soil particles to sink and the oil

Exhibit 5. Washing Test Data, Thunder Bay Harbour, Ontario, Sediment.

BioGenesis Sediment Washing, 6/1/93
Pilot testing for Environment Canada, Wastewater Technology Centre, Great Lakes Cleanup Program

			SOLIDS (Parts per Million)			LIQUID (Parts per Million)
TEST		UNTREATED	CYCLE 1	CYCLE 2	CYCLE 3	WASTEWATER
Oil & Grease		91,600	NR	NR	3,940	NR
Semivolatile Petroleum HC		21,000	NR	NR	2,200	NR
Total Petroleum Hydrocarbon		4,770	4,840	1,670	400	NR
Total Organic Content		11.5%	NR	NR	2.9%	NR
CAS No.	COMPOUND					
91-20-3	Naphthalene	1,400	1 ,000	170	73	14
85-01-8	Phenanthrene	770	700	130	88	2.2
206-44-0	Fluoranthene	460	430	83	59	1.0
83-32-91	Acenaphthene	340	290	55	34	1.2
29-0-0	Pyrene	320	300	59	44	0.8
86-73-7	Fluorene	260	230	45	30	0.8
56-55-3	Benzo(a)anthracene	110	100	23	19	0.2 E
120-12-7	Anthracene	97 E	90 E	21	16	0.2 E
205-99-2	Benzo(b)fluoranthene	97 E	88 E	24	19	ND
50-32-821	Benzo(a)pyrene	78 E	61 E	15	12	ND
8-01-9	Chrysene	69 E	68 E	15	12	0.1
207-08-91	Benzo(k)fluoranthene	42 E	40 E	6.5 E	6.1	ND
91-24-21	Benzo(g,h,i)perylene	36 E	32 E	5 E	3.9	ND
93-39-5	Indeno(1,2,3-cd)pyrene	33 E	30 E	5.9 E	5	ND
208-96-8	Acenaphthylene	15 E	ND	2.4 E	1.5	ND
53-70-3	Dibenzo(a,h)anthracene	ND	ND	ND	1.4	ND
	16 PAHs	4,079	3,429	652	416	21
CUMULATIVE REMOVAL PERCENTAGE			15.9%	84.0%	89.8%	NA

ND = Below detection limits NA = Not applicable
E = Estimated concentration NR = Not requested
Note: Removed oils floated on the wastewater surface. Testing not designed for mass balance determination.

removed to rise to the water surface, where it is skimmed for reclamation or disposal. Following drainage of the wash water, the clean soil is evacuated by raising the unit's dump mechanism. Processed soil contains a moisture level of 20 to 30 percent depending on the soil matrix.

The gondola is equipped with an emission control system to trap volatile organic compounds (VOCs) if a volatile contaminant is being cleaned. Process air passes first through the slurry, and then through a chilling unit. This traps VOCs in a collection tank. Carbon filter beds provide a final polishing effect before the air is released to the atmosphere.

SEDIMENT PROCESS TESTING

Under the auspices of Wastewater Technology Centre's (WTC's) Contaminated Sediment Treatment Technology Program, BioGenesis contracted to test its washing technology on sediment from a former wood preserving site at Thunder Bay, Ontario. This site, containing 20,000 cubic meters, is one of 43 "areas of concern" identified by the International Joint Commission, a joint U.S.-Canadian body tasked to administer the Great Lakes Water Quality Agreement. The major contaminants on the site are PAHs, with low levels of PCBs, phenols, and several metals. The PAHs were determined to be the primary target of the washing test. Typical sediment grain size (81 percent) was less than 38 microns (see **Exhibit 4**).

Test sediment was selected from the worst contaminated areas of Thunder Bay, as determined by surveys in 1984, 1988, and 1992. In early June 1993, BioGenesis performed the testing under the audit of a Canadian representative of WTC. Split-sample procedures were followed to maintain testing integrity. Independent testing of all samples was conducted for BioGenesis by Galson Laboratories, Inc., of Syracuse, New York. The testing was originally planned as a bench-scale test. However, due to the high pressures involved and inability to effectively model the process parameters in bench-scale equipment, the testing used pilot-scale equipment capable of processing 1.5 to 2 cubic yards an hour. **Exhibit 5** shows the cumulative reduction of contamination levels with each wash cycle for PAHs (cycle 1—16 percent; cycle 2—84 percent; and cycle 3—90 percent). There appear to be no technical obstacles to fine-tuning the scrubbers to increase removal effectiveness per cycle by up to 20 percent and none to adding additional scrub cycles without diminishing the throughput rate. Predicted process efficiency with these changes is at least 98 percent. Despite relatively high organic content, PAH extraction efficiencies were consistent with testing results for oil and grease and semivolatile hydrocarbons. **Exhibit 6** illustrates this correlation. **Exhibits 7** and **8** show individual compound results for the PAHs that were the primary extraction target. Note that the pattern of removal effectiveness was consistent among the 16 PAHs. The extraction level averaged 90 percent with negligible variation in extraction efficiencies among different contaminants.

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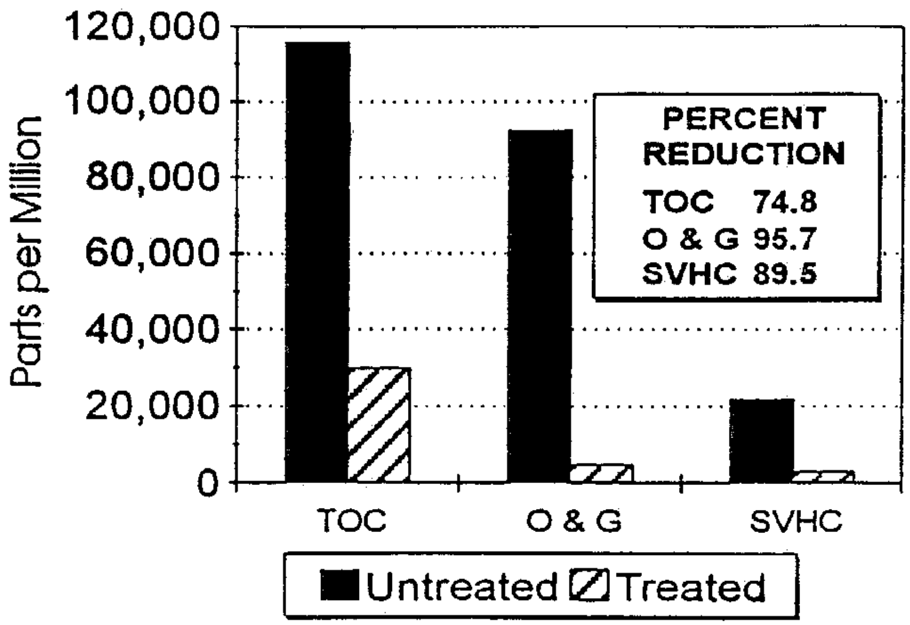
SOIL WASHING PROCESS TESTING

To efficiently wash soils with grain sizes larger than approximately 0.5 mm, the BioGenesis process uses equipment that takes advantage of the lower bonding energy of organics and inorganics on larger particles. This equipment uses heat, water, cleaner, and air mixing to remove and float hydrophobic pollutants or to solubilize compounds that are heavier than water.

The soil washing equipment was demonstrated in the U.S. EPA SITE program during November 1992. About 3,800 tons of soil were contaminated with up to 3 percent heavy crude oil at a refinery. Due to extended weathering, the soil contained only trace levels of benzene, toluene, ethylbenzene, and xylene (BTEX). Total recoverable petroleum hydrocarbons (TRPH) was selected as the contaminant group of concern. **Exhibit**

Exhibit 6. Overall Removal Effectiveness: Pilot Testing on Thunder Bay Harbour, Ontario, Sediment.

Total Organic Content, Oil and Grease, Semivolatile Hydrocarbons



Total Petroleum Hydrocarbons, Polyaromatic Hydrocarbons

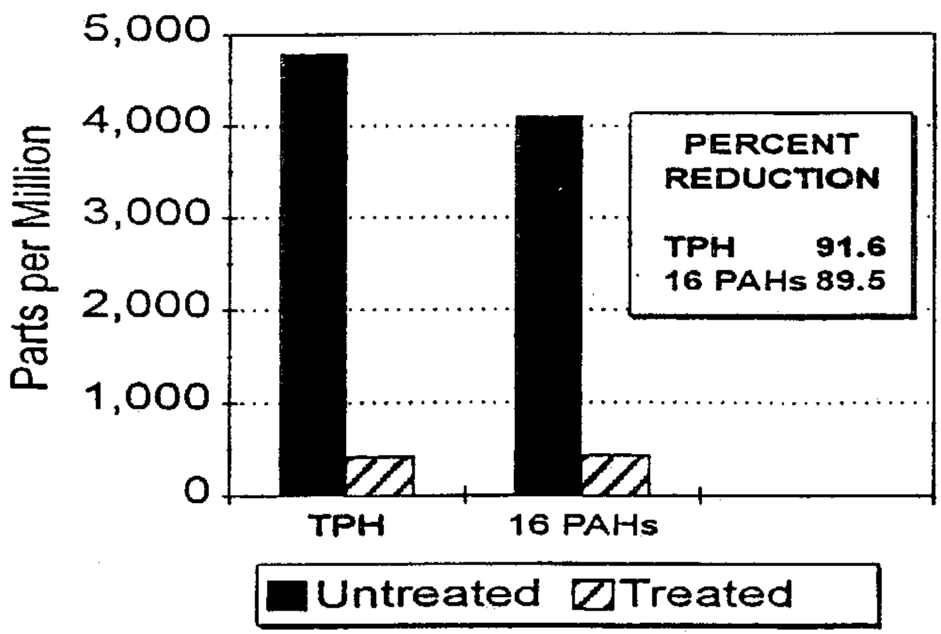


Exhibit 7. PAH Removal Effectiveness: Pilot Testing on Thunder Bay Harbour, Ontario, Sediment.

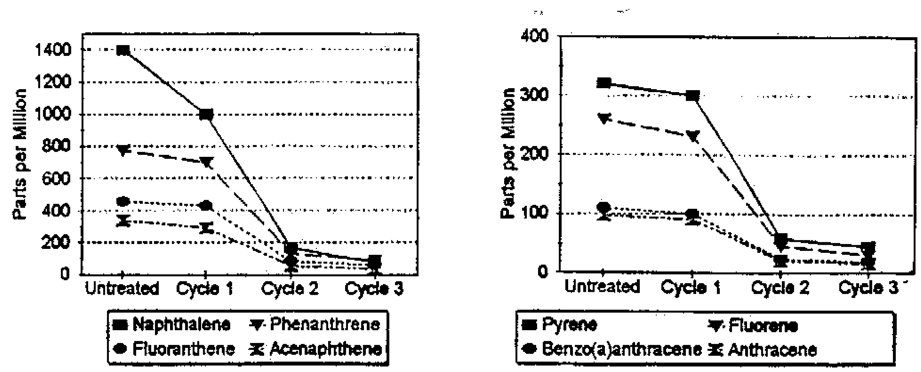
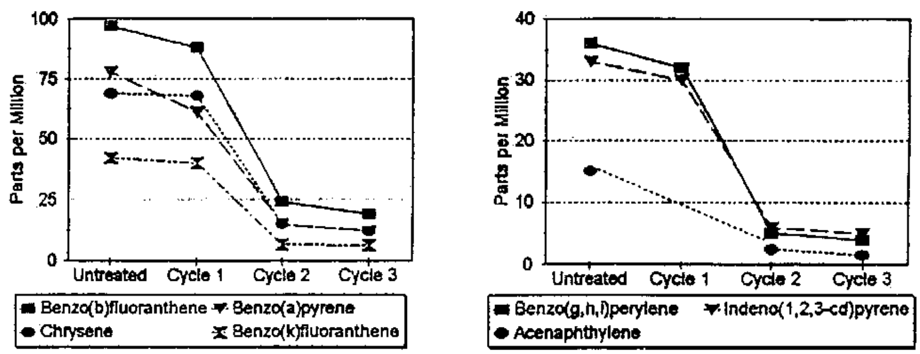


Exhibit 8. PAH Removal Effectiveness: Pilot Testing on Thunder Bay Harbour, Ontario, Sediment.

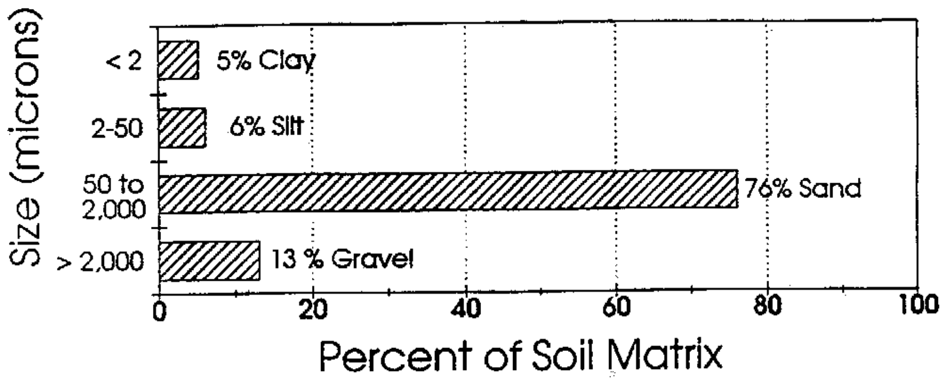


9 shows the particle size distribution of the soil matrix. Effective grain size was approximately 50 microns (10 percent smaller and 90 percent larger).

Based on an initial contamination level of 30,800 ppm, extraction effectiveness for washing alone was 85 to 90 percent with subsequent biodegradation raising that to an overall effectiveness of 95 to 98 percent. These results are illustrated in **Exhibit 10**. Results were tabulated for soil fractions greater than, and less than, 300 microns. As was expected, after the initial washing, greater extraction (91 percent) was achieved on the larger fractions than on the smaller particle sizes. Noteworthy, however, is that even on the fines fraction, 85 percent extraction resulted.

Both the larger and smaller fractions were then monitored for biodegradation of residual contamination not removed in the washing. This monitoring was to ascertain the degree to which the washing chemicals enhanced and facilitated biodegradation. As shown in Exhibit 10, rapid biodegradation was observed on the fines fraction during the

Exhibit 9. Particle Size Distribution of Crude-Oil-Contaminated Refinery Soil.



succeeding two weeks, with a reduction of the "after-washing" level of 52 percent after seven days and a cumulative reduction of the after-washing level by 71 percent at the end of two weeks.

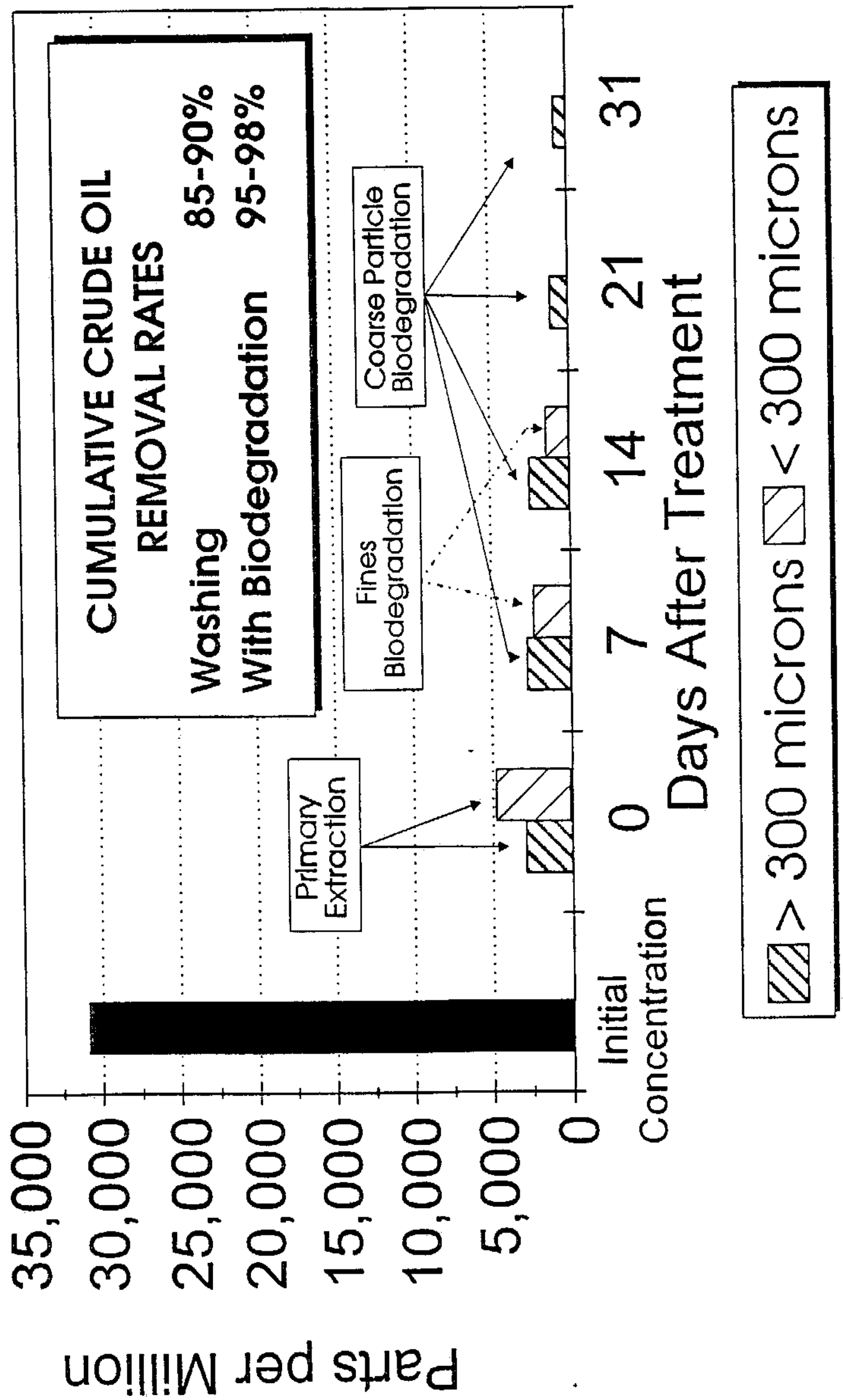
Biodegradation of the larger size fractions representing over 85 percent of the soil was monitored for 31 days. At the 7-, 14-, 21-, and 31-day points, cumulative reductions from the after-washing level were tested as 7 percent, 14 percent, 64 percent, and 75 percent, respectively. After washing and one month of biodegradation, washing and biodegradation had removed 95 to 98 percent of the crude oil contamination in both the coarse and fines fractions. EPA testing verified the reproducibility of washing results at constant operating conditions.

Direct conclusions drawn from the SITE demonstration include (1) a general range of washing effectiveness from 85 percent to 95 percent, (2) effective biodegradation induced by BioGenesis chemicals, and (3) the ability of the BioGenesis process to consistently remove weathered heavy oils from soil that has an effective grain size of 50 microns. Significant inferences from the SITE demonstration are that the process will have higher effectiveness on pollutant structures less complex than weathered crude oil (e.g., diesel fuel) and that it can also be applied successfully to other types of organic contaminants, such as PCBs, dioxins, and pesticides.

CONCLUSION

BioGenesis soil and sediment washing combines equipment design factors (temperature, pressure, friction, duration) with proprietary chemical blends tailored to specific site conditions. The process achieves high extraction levels on oils and, by extension, on most organic pollutants in both large- and small-grain soils. Additionally, the equipment's relatively small size and its mobility promise economical treatment for the large number of sites below the economic threshold of conventional soil

Exhibit 10. Overall Removal Effectiveness on Crude-Oil-Contaminated Refinery Soil.



washing. Finally, negligible undesirable by-products, high processing rates, the absence of air pollution, and elimination of the necessity to transport contaminated material off-site all point to reduced cost and increased acceptability of this technology by both regulatory authorities and public interest and environmental groups. ■